Enhanced Droplet Nucleation in Styrene Miniemulsion Polymerization. 3. Effect of Shear in Miniemulsions That Use Cetyl Alcohol as the Cosurfactant

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ABSTRACT: The effect on the polymerization kinetics of the level of shear imparted during homogenization of styrene miniemulsions prepared with cetyl alcohol was studied. It was noted that, at relatively low levels of shear, predissolving polystyrene into the monomer prior to homogenization did not result in an enhancement in the kinetics. At high levels of shear, there was a large enhancement in the rate of polymerization that results from predissolving polymer. These conflicting results were correlated to droplet stability measurements. Droplet sizes formed in the size region produced by the low levels of shear have been shown to be stable with time while the droplet sizes formed by the high level of shear have been shown to be unstable with time. The combination of the kinetic results and the droplet stability measurements was taken as evidence that the dominant mechanism causing "enhanced droplet nucleation" is the preservation of the droplet number prior to the polymerization. Numerous results are also presented that show that the rate of miniemulsion polymerization is directly proportional to the droplet number available at the time of polymerization. With a better understanding of the nucleation mechanisms in miniemulsion polymerization, future formulations can be designed to ensure all nucleation in these systems occurs in the monomer droplets.

Introduction

The dominant site for nucleation in miniemulsion systems is the monomer droplets.[1−3] Therefore, it is not surprising that the kinetics of a miniemulsion system is a strong function of the number of monomer droplets created during the homogenization step. Many researchers have noted that as the level of homogenization is increased, the rate of polymerization also increases. Tang[4] reported that the rate of polymerization increased and the particle size decreased in a styrene miniemulsion stabilized with hexadecane when the Microfluidizer (a relatively high shear device) was used compared to the Omni Mixer (a relatively low shear device). Rodriguez[5] observed that as the sonification time increased, the particle size decreased in miniemulsion copolymerizations of styrene and methyl methacrylate that used hexadecane as the cosurfactant. In fact, even in conventional emulsion polymerizations, Durbin et al.[6] noted that the relative amount of droplet nucleation increases as the emulsion is subjected to higher levels of shear prior to the reaction (although droplet nucleation remained a relatively insignificant nucleation process at all levels of shear).

Many researchers have noted that the monomer droplet size changes as a function of time for miniemulsions that use cetyl alcohol as the cosurfactant. Ugelstad et al.[7] measured the amount of free surfactant as a function of time for miniemulsions prepared using cetyl alcohol as the cosurfactant. It was reported that the droplet size degraded up to a constant plateau value. Similar behavior has been observed by Miller et al.[8] using capillary hydrodynamic fractionation and by Chern and Chen[9] using dynamic light scattering.

Miller et al.[10−12] have reported that predissolving a small quantity of polystyrene into the monomer prior to homogenization results in large enhancements in the rate of polymerization and the number of droplets nucleated in styrene miniemulsions that use cetyl alcohol as the cosurfactant. The kinetic behavior found in these systems was termed "enhanced droplet nucleation". In all experiments, the miniemulsions were created using the Microfluidizer, which is an extremely efficient shear device. In a previous paper, Blythe et al.[13] suggested that this phenomenon is due to the thermodynamic preservation of the monomer droplets prior to the initiation of polymerization due to the presence of the predissolved polymer. In the absence of predissolved polymer, Ostwald ripening can cause the elimination of the smaller droplets via diffusion of monomer to the larger droplets. Thus, both the droplet size distribution and the initial number of droplets change upon aging of the miniemulsion. Ostwald ripening may still be operative in the presence of predissolved polymer, which may lead to a change in the droplet size distribution. However, the initial number of droplets will be preserved due to the water insolubility of the high molecular weight polymer.

This paper will examine the effect of changing the level of shear imparted to create a styrene miniemulsion when cetyl alcohol is used as the cosurfactant. Miniemulsion systems containing predissolved polymer will be contrasted with miniemulsion systems not containing any predissolved polymer. Of specific interest will be whether the "enhanced droplet nucleation" phenomenon will be present when a droplet size is produced during homogenization which is above the instability regime reported for styrene miniemulsions prepared with cetyl alcohol. If the droplet size produced during homogenization is above the unstable regime and these systems do not exhibit an enhancement in the rate of polymerization and number of droplets nucleated, this will be further evidence that the cause of "enhanced droplet nucleation" is the preservation of droplet number.

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Table 1. Basic Recipe for the Polymerizations

ingredient	amount	grams
styrene	19.8−20.0 parts	138.6−140
polystyrene [a]	0.0−0.2 parts	0.0−1.4
distilled water	80 parts	560.0
sodium lauryl sulfate [b]	10 mM	1.595
cetyl alcohol [b]	30 mM	4.023
sodium bicarbonate [b]	1.33 mM	0.062
potassium persulfate [b]	1.33 mM	0.1975

[a] Not present in all recipes. [b] Based on the aqueous phase.

Table 2. Experimental Variables Studied

expt identifier	1% polymer	homogenizer	time/passes
LE99	no	Omni Mixer	15 min
LE100	yes	Omni Mixer	15 min
LE101	no	Sonifier	1 min
LE102	yes	Sonifier	1 min
LE108	no	Sonifier	5 min
LE107	yes	Sonifier	5 min
LE104	no	Sonifier	15 min
LE103	yes	Sonifier	15 min
KPS4	no	Microfluidizer	10 passes
LE47	yes	Microfluidizer	10 passes

Experimental Section

Materials. Styrene (Aldrich) was distilled under a reduced pressure of 0.02 atm and stored at −5 °C for later use. Sodium lauryl sulfate, SLS (BDH Biochemical, Ultrapure Bioreagent, 99% pure), was used as received. Potassium persulfate, KPS (FMC Corp.), was recrystallized from deionized water and dried under vacuum. Cetyl alcohol, CA (Aldrich), and sodium bicarbonate (Fisher) were used as received. Polystyrene was prepared by anionic polymerization (M_n = 39 000 g/mol; M_w = 45 100 g/mol; hydrogen end group). Deionized water was used in the experiments.

Recipe and Procedures. The ingredients used in the formulation of the miniemulsions are given in Table 1. First, an aqueous gel phase was created by mixing the SLS, CA, distilled water (less 1% of the water which was saved to dissolve the initiator), and $NaHCO_3$ for 2 h at 70 °C. The gel phase was then cooled under agitation and sonified (Branson Sonic Power Co.) at 50% duty, power 7, and pulsed for 60 s. When polystyrene was used, it was predissolved in the monomer until all visible traces of the polymer disappeared. The oil phase was then added to the gel phase and mixed in a beaker for 20 min using a stir bar. At this point, one of three methods for homogenization was used. In the first method, an Omni Mixer (Ivan Sorvall, Inc.), operated at about 16 000 rpm for 15 min, was used to provide the shear. The emulsion was separated into three equal volumes for processing due to the small capacity of the Omni Mixer. Also, to minimize the temperature increase in the system during the operation of the Omni Mixer, an ice bath was applied to the flask containing the emulsion. The second method for providing homogenization was sonification. The Sonifier was used at 50% duty and power 7 for either 1, 5, or 15 min depending upon the experiment. A stirring bar was used in the vessel containing the emulsion to ensure macromixing. Again, an ice bath was applied to the vessel to reduce any temperature buildup during homogenization. In the third method, the emulsion was first sonified for 60 s at 50% duty, power 7, and pulsed. Finally, the crude miniemulsion was passed through the Microfluidizer (Microfluidics Corp.) for 10 passes at 80 psi inlet pressure. For all three homogenization techniques, the resulting miniemulsion was then added to the Mettler RC1 calorimeter where the KPS/water solution was added after heating the miniemulsion to 70 °C. The Mettler RC1 calorimeter provides a virtually continuous measurement of the heat of reaction that can be directly related to the rate of polymerization. Table 2 lists the variables studied in this paper. Particle size measurements were made by capillary hydrodynamic fractionation (CHDF) using a Matec CHDF-1100 unit.

Homogenizing Equipment. The Omni Mixer produces high-speed mixing to shear the emulsion near the impeller. The sonifier converts electrical energy to mechanical energy by producing rapid local pressure variation near the sonifier tip. The emulsion is subjected to the resulting shear and cavitation forces near the tip. The Microfluidizer (MP110-A) works by pumping the emulsion to high pressure (6000−8000 psi) via a piston pump. The emulsion is then forced through the interaction chamber where the stream is split into two microchannels. In the microchannels, the streams accelerate to approximately 30 000 cm/s and are impacted against an orifice plate which acts to break up the dispersed phase by shear and collision forces. The most significant breakup of the droplets occurs when the two streams are recombined in the orifice plate due to the shear, cavitation, and impact forces. The resulting droplet size for each piece of equipment is different. Homogenizing with the Omni Mixer results in the coarsest miniemulsion, the Sonifier produces broad, intermediate droplet sizes, and the Microfluidizer produces the finest droplet size.[4]

Results and Discussion

The Experimental Rationale for Experiments with the Omni Mixer. Miller et al.[8] have shown, using capillary hydrodynamic fractionation (CHDF), that miniemulsion droplets stabilized with cetyl alcohol as the cosurfactant and formed using the Microfluidizer exhibit droplet size growth from an initial value of 80 nm to a plateau value of about 175 nm. If polymer acts to preserve the initial droplets such that no degradation phenomenon occurs, there will be a much higher droplet number available for polymerization when polymer is predissolved into the miniemulsion, and this will result in higher rates of nucleation and thus polymerization. The CHDF results indicated that larger droplets were effectively stabilized by the cosurfactant, cetyl alcohol. If the initial shear imparted to the miniemulsion is not great enough to reduce the initial droplet size to the region observed in the previous CHDF work where droplets degrade, the system should not undergo this droplet growth phenomenon. Thus, if predissolving polymer in the monomer prior to homogenization is acting as an additional stabilizer to the miniemulsion droplets, miniemulsions that are formed with droplet sizes above the unstable regime seen by the CHDF would not exhibit the “enhanced droplet nucleation” phenomenon. However, if predissolving polymer in the droplets caused an increase in the radical capture efficiency of the droplets, an enhancement in the rate of polymerization should still be seen even for the larger size droplets. Previous work has shown that, by using the Omni Mixer to homogenize the miniemulsion droplets in a 5 mM SLS/20 mM hexadecane system, a final latex with an average volume diameter of 344 nm results.[4] This is an indirect indication the average droplet diameter produced with the Omni Mixer is above 175 nm, which Miller et al.[8] have shown is the critical size when droplets are no longer unstable to droplet growth when cetyl alcohol is used as the cosurfactant.

It has been suggested the enhancement in the rate of polymerization when polymer is predissolved in the miniemulsion in systems homogenized with the Microfluidizer is due to a greater number of droplets being formed in the presence of polystyrene. This is not likely, since it has been shown that the presence of polymer in the monomer will increase the viscosity of the phase to be dispersed into droplets.[13] This would result in less droplets being formed upon homogenization (which would actually cause a reduction in the rate of polymerization). Thus, if polymer affects the droplet distribution, it will be caused by the extra stabilization of the formed droplets after homogenization and not by chang-

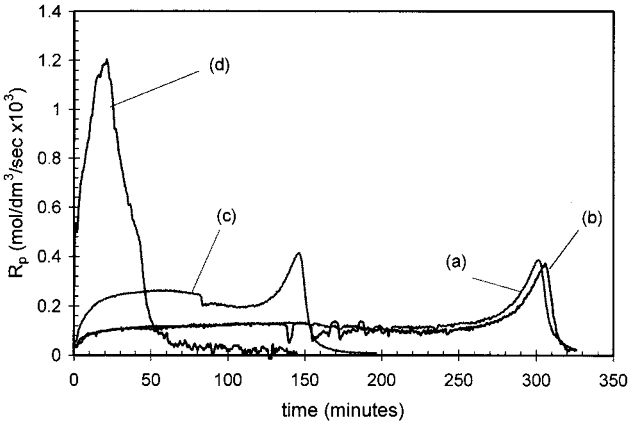

Figure 1. Effect of predissolving 1% polystyrene on the rate of polymerization in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase and homogenized with either the Omni Mixer or the Microfluidizer: (a) Omni Mixer with no polymer; (b) Omni Mixer with 1% polymer; (c) Microfluidizer with no polymer; and (d) Microfluidizer with 1% polymer; [KPS] = 1.33 mM; polystyrene M_n= 39 000 g/mol and H terminated; T_r = 70 °C.

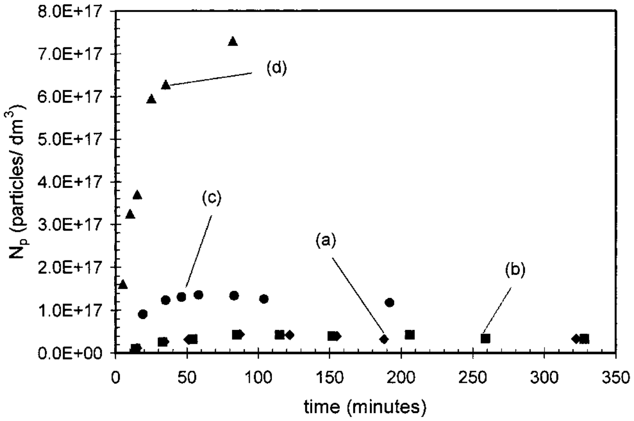

Figure 2. Effect of predissolving 1% polystyrene on the number of particles versus time in the polymerization of styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase and homogenized with either the Omni Mixer or the Microfluidizer: (a) Omni Mixer with no polymer (◆); (b) Omni Mixer with 1% polymer (■); (c) Microfluidizer with no polymer (●); and (d) Microfluidizer with 1% polymer (▲); [KPS] = 1.33 mM; polystyrene M_n = 39 000 g/mol and H terminated; T_r = 70 °C.

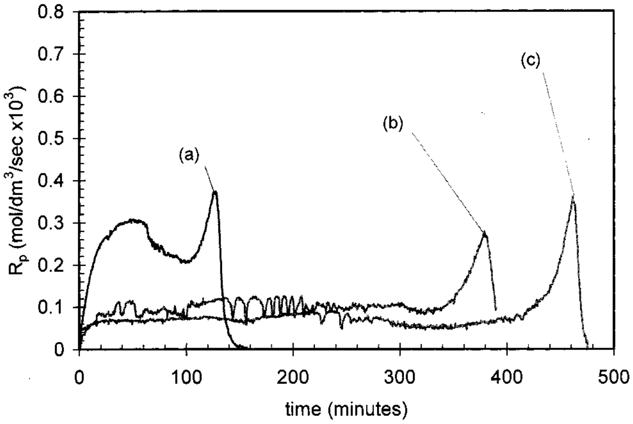

Figure 3. Effect of increasing sonification time on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase that contain no predissolved polymer: (a) 15 min, (b) 5 min, and (c) 1 min; [KPS] = 1.33 mM; T_r = 70 °C.

ing the number of droplets formed during homogenization.

Miniemulsion Kinetics with Varying Levels of Shear. The effect on the rate of polymerization of predissolving 1% polymer in the monomer prior to homogenization with either the Omni Mixer or the Microfluidizer in miniemulsions formed using cetyl alcohol as the cosurfactant is shown in Figure 1. The results for the systems formed with the Omni mixer are significantly different from what was seen when a more efficient homogenization device, the Microfluidizer, was used. Miniemulsions using cetyl alcohol as the cosurfactant and formed with the Microfluidizer show a significant enhancement in the rate of polymerization when polymer is predissolved in the monomer droplets. However, when the Omni Mixer is used, this enhancement is not seen. This result is in agreement with the explanation that "enhanced droplet nucleation" is due to a change in the droplet number resulting from the addition of polymer prior to polymerization.

Figure 2 shows the corresponding evolutions of the number of particles versus reaction time for the above experiments. There is virtually no effect of predissolving 1% polymer into the miniemulsion on the number of particles nucleated versus reaction time when the system is homogenized with the Omni Mixer. However, when the miniemulsion is homogenized with the Microfluidizer, there is a significant enhancement in the number of particles nucleated when polymer is predissolved into the miniemulsion. Thus, the rate of polymerization data shown in Figure 1 can be directly related to the number of particles nucleated versus time shown in Figure 2. The difference between the two methods of applying the energy (Microfluidizer and Omni Mixer) should be reflected in the droplet size distribution. When the miniemulsions are created with the Microfluidizer, the cetyl alcohol is unable to preserve the small size droplets formed by the high shear device. The reason for the enhancement in the number of particles nucleated when polymer is predissolved is that the miniemulsion droplets (particularly the smaller size fraction of the distribution—approximately less than 80 nm) are preserved by the presence of polymer due to the thermodynamic equilibrium maintained between monomer and polymer in each droplet (as predicted by the well-known Morton equation). However, when the Omni Mixer is used, the mixed emulsifier system is able to stabilize the larger droplets created by the low shear device. Thus, the ability of polymer to preserve the droplet number will not exhibit a noticeable effect on the kinetics since in this case the smaller droplets are not formed in the first place. For miniemulsions formed with the Omni Mixer, cetyl alcohol is able to provide thermodynamic stabilization of the droplet size in the absence of predissolved polymer since the small size droplets do not exist (compared to the Microfluidizer).

Effect on Kinetics of Varying Sonification Time. Figure 3 shows the effect of increasing sonification time on the rate of polymerization versus time in miniemulsions stabilized with cetyl alcohol that do not contain predissolved polymer. It is apparent that increasing the sonification time (up to 15 min) causes an increase in the rate of polymerization. It is expected that increasing the sonification time will increase the number of droplets formed during the homogenization step since the sonifier tip is unable to apply an even shear to the whole system (especially at the lower sonification times). Thus,

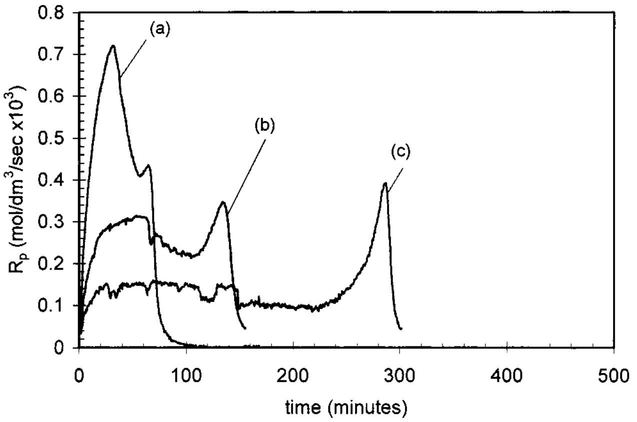

Figure 4. Effect of increasing sonification time on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase that contain 1% predissolved polymer: (a) 15 min; (b) 5 min; and (c) 1 min; [KPS] = 1.33 mM; polystyrene M_n = 39 000 g/mol and H terminated; T_r = 70 °C.

the fact that the rate of polymerization increased with the number of droplets formed is a strong indication that droplet nucleation is the predominant mechanism for particle nucleation. This is important since experimental results indicate the possibility that homogeneous nucleation may be responsible for particle nucleation in the miniemulsion systems formed with relatively low shear. The flat rate of polymerization versus time curves and the narrow particle size distributions (discussed at a later point in this paper) have both been observed in systems controlled by homogeneous nucleation.[14] However, if homogeneous nucleation was the dominant form of nucleation in miniemulsion systems formed with low shear, the rate of polymerization should decrease with increasing droplet number. This would be caused by a decrease in the level of free surfactant as the droplet surface area increases. However, the experimental data show the opposite effect, so these systems must undergo predominantly droplet nucleation (not homogeneous nucleation).

Figure 4 shows the effect of increasing the sonification time on the rate of polymerization curves in miniemulsions stabilized with cetyl alcohol that contain 1% predissolved polymer. As seen in the miniemulsions that do not contain predissolved polymer, the rate of polymerization increases as the droplet number formed during homogenization increases. Also, comparing Figures 3 and 4 reveals that miniemulsion systems containing a small amount of predissolved polymer always exhibit faster rates of polymerization. This is the same behavior that is observed when polymer is predissolved into miniemulsions formed with the Microfluidizer. Miller et al.[8] have shown that producing miniemulsions with cetyl alcohol by sonification results in droplet sizes that fall in the unstable regime. Thus, predissolving polymer into the initial miniemulsion will act to preserve the droplet number formed during homogenization and thus cause the enhancement in the rate of polymerization.

Figures 5 and 6 show the number of particles versus time behavior for the reactions presented in Figures 3 and 4, respectively. Particle size measurements were made with the CHDF. As expected, the miniemulsions containing 1% polymer have greater numbers of particles formed than the miniemulsions containing no predissolved polymer at identical sonification times. Also, the number of particles nucleated increases as the number of droplets formed during homogenization increases. In all cases, it is apparent that the number of particles formed during the polymerization is directly related to the number of droplets available for polymerization.

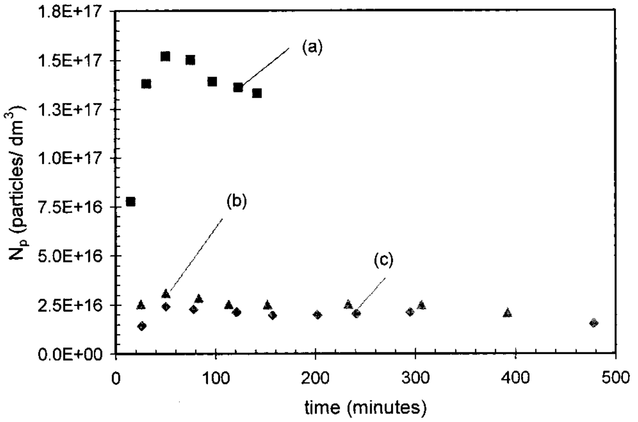

Figure 5. Effect of increasing sonification time on the number of particles versus time in the polymerization of styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase that contain no predissolved polymer: (a) 15 min (■); (b) 5 min (▲); and (c) 1 min (◆); [KPS] = 1.33 mM; T_r = 70 °C.

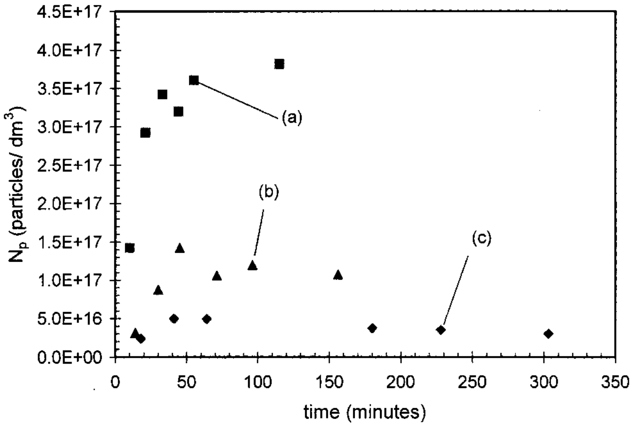

Figure 6. Effect of increasing sonification time on the number of particles versus time in the polymerization of styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase that contain 1% predissolved polymer: (a) 15 min (■); (b) 5 min (▲); and (c) 1 min (◆); [KPS] = 1.33 mM; T_r = 70 °C.

Table 3. Particle Size Measurements Made by TEM for Miniemulsions Created with 60 s of Sonification

sample	polym	conversion (%)	polym time (min)	D_n (nm)	D_w (nm)	PDI
LE101-1	no	3.8	26	84.3	92.8	1.10
LE101-3	no	11.2	78	119.6	125.8	1.12
LE101-5	no	25.4	157	171.9	182.9	1.06
LE101-7	no	41.6	241	238.9	254.5	1.07
LE101-F	no	91.4	475	337.0	364.3	1.08
LE102-1	yes	3.7	18	69.2	92.2	1.33
LE102-3	yes	18.1	64	114.7	123.4	1.08
LE102-5	yes	51.4	180	205.0	225.4	1.10
LE102-F	yes	90.9	303	260.4	268.0	1.07

Table 3 lists the particle size data measured by TEM for samples withdrawn during the reaction at various times for miniemulsions prepared with and without added polymer, stabilized with cetyl alcohol, and created with 60 s of sonification. As expected, the miniemulsion formed with 1% polymer, which exhibited faster rates of polymerization, resulted in a smaller final particle size. The polydispersity indexes of the resulting latexes

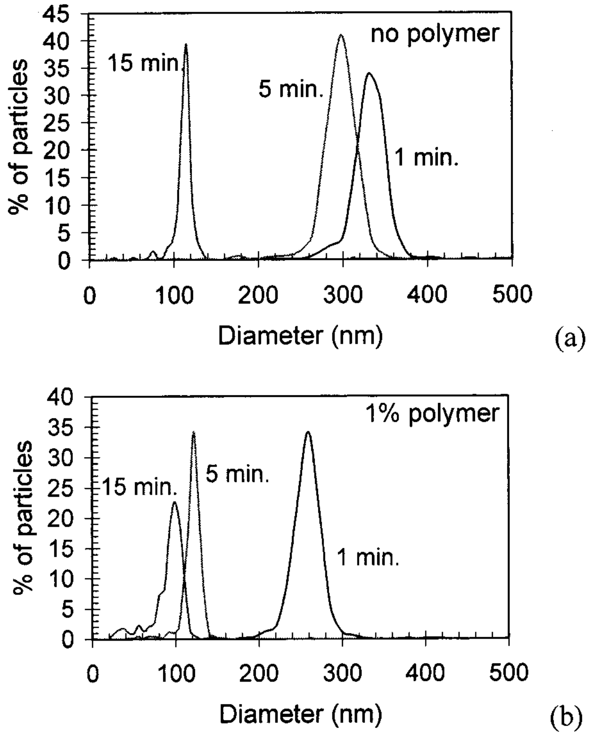

Figure 7. Effect of varying the level of sonification on the final particle size distributions measured by TEM for the polymerization of styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) no predissolved polymer—1, 5, and 15 min sonification; and (b) 1% predissolved polymer, M_n = 39 000 g/mol and H terminated polystyrene—1, 5, and 15 min sonification; [KPS] = 1.33 mM; T_r = 70 °C.

are relatively narrow over the entire reaction period although all the samples contained an extremely small amount of off-size particles greater than 400 nm (~1 large particle per 500 particles in the main peak). The narrow particle size distributions indicate that nucleation of monomer droplets occurs rapidly in the reaction and ends at a relatively low conversion. Miniemulsions stabilized with cetyl alcohol and formed using the Microfluidizer exhibit long periods of droplet nucleation up to at least 40% conversion.[14] Polymerization of similar miniemulsions but now containing 1% predissolved polymer results in bimodal particle size distributions.[14] This particle size bimodality is not noted in similar systems formed with low sonification time. It is suggested that the different behavior seen in the system with 60 s sonification is due to the extremely low number of droplets present for nucleation. Since the droplet number is low, nucleation of droplets is complete at early conversions. Thus, the low rates of polymerization in these systems are due to a low droplet number available for polymerization and not inefficient entry of free radicals into the miniemulsion droplets.

Figure 7 shows the particle size distributions measured by TEM for the final latexes resulting from the miniemulsion systems subjected to 1, 5, and 15 min of sonification and prepared with and without added polymer. The corresponding particle size data are shown in Table 4. As expected, the particle size of the final latexes decreases with increasing sonification time. Also, the particle sizes for the samples containing 1% polymer are significantly smaller than the parallel samples prepared without predissolved polymer. The particle size decreases with increasing sonification time and the presence of polymer because the droplet number available for polymerization is higher in these systems for reasons discussed previously. Careful examination of Figure 7 reveals a tail of small size particles in the system that contains predissolved polymer and is sonified for 15 min. This tail is similar to what Miller et al.[11] observed in miniemulsions that contained predissolved polymer and were homogenized with the Microfluidizer. The most likely source of the small particles is the fraction of the droplets that are never entered by radicals. Indeed, the size of these particles is similar (~30 nm) to the size measured by Miller et al.[10] for particles formed by stripping the monomer from miniemulsion droplets (formed using cetyl alcohol and containing 1% predissolved polymer) prior to initiation. The ultimate fate of the unentered droplets that contain predissolved polymer is the donation of all the monomer to the growing polymer particles. This leaves small particles that contain the predissolved polymer and cetyl alcohol. This small tail of particles caused by the unentered droplets is only present in the miniemulsion that was homogenized for 15 min. The tail is not found in the miniemulsions containing predissolved polymer that were homogenized for 1 and 5 min because the droplet surface area formed during homogenization is significantly less than the miniemulsion homogenized for 15 min. In the systems with a lower surface area, the available number of radicals per droplet will be higher. Therefore, in these systems all the droplets are entered by radicals before the droplets completely donate their monomer to the growing polymer particles.

Table 4. Particle Size Measurements Made by TEM for Miniemulsions Created with Varying Degrees of Sonification

sample	polymer	homog time	D_n (nm)	D_w (nm)	PDI
LE103	yes	15	92.2	100.9	1.09
LE104	no	15	112.9	119.7	1.06
LE107	yes	5	120.6	125.7	1.04
LE108	no	5	298.2	316.2	1.06
LE102	yes	1	260.4	268.0	1.07
LE101	no	1	337.0	364.3	1.08

Another interesting feature of Figure 7 is the average particle size of the miniemulsions subjected to 5 min of sonification. When polymer is predissolved in the miniemulsion, the average particle size in the miniemulsion sonified for 5 min is similar to the miniemulsion that was sonified for 15 min. However, when no polymer is predissolved, the average particle size is close to the miniemulsion that was sonified for 1 min. It is suggested that this behavior is a consequence of the instability of the small size droplets formed during sonification. When polymer is predissolved into the system, all the droplets formed during homogenization are preserved by the predissolved polymer. Therefore, the number of droplets formed during homogenization (which will increase with increasing sonification time) will be available for polymerization. However, when no polymer is predissolved, the small droplets are unstable to degradation by Ostwald ripening. As a result, the number of droplets formed during homogenization will not be the same quantity that is available for polymerization. Furthermore, it is suggested that when a significant quantity of the monomer is contained in the larger droplets (those not affected by the sonifier tip), there is a large driving force for monomer diffusion from the small to large droplets due to Ostwald ripening. This diffusion is inherent in all emulsion systems because the small droplets have higher chemical potentials than the larger

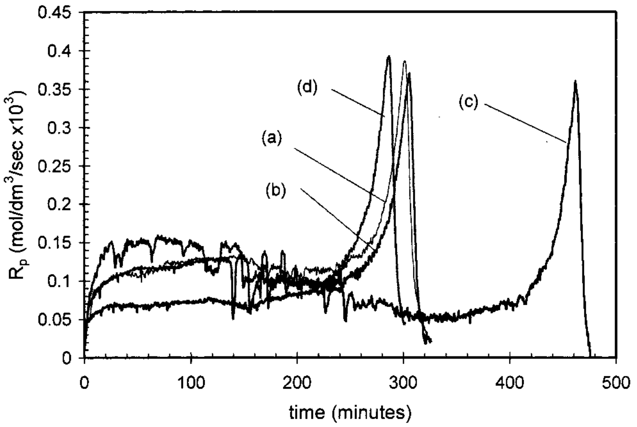

Figure 8. Effect of predissolving 1% polystyrene on the rate of polymerization in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase and homogenized with either the Omni Mixer or 60 s of sonification: (a) Omni Mixer and no polymer; (b) Omni Mixer and 1% polymer; (c) 60 s sonification and no polymer; and (d) 60 s sonification and 1% polymer; [KPS] = 1.33 mM; polystyrene M_n = 39 000 g/mol and H terminated; T_r = 70 °C.

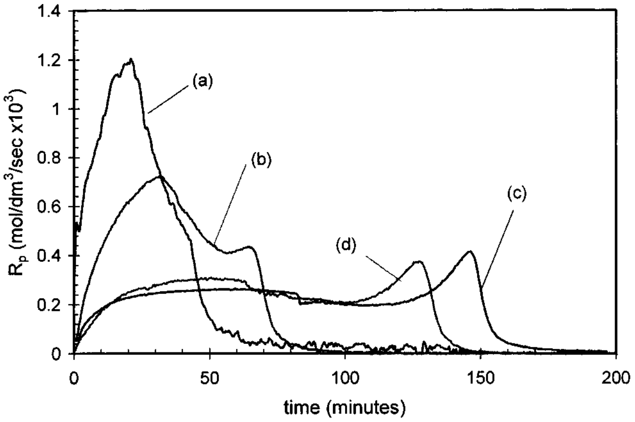

Figure 9. Effect of using either the Microfluidizer or Sonifier on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) Microfluidizer and 1% polymer; (b) Sonifier for 15 min and 1% polymer; (c) Microfluidizer and no polymer; and (d) Sonifier for 15 min and no polymer; [KPS] = 1.33 mM; polystyrene M_n = 39 000 g/mol and H terminated; T_r = 70 °C.

droplets due to the variation of Gibbs free energy with droplet size. Thus, to minimize the free energy in the system, small droplets tend to disappear with time by diffusion into the larger droplets. Indeed, Higuchi and Misra[16] have shown that as the difference in droplet sizes increases in an emulsion system and an effective cosurfactant is not present in the system, the rate of degradation of the small size droplets increases. In the system that was sonified for 15 min, all of the miniemulsion has been proposed to be exposed to the maximum shear under the sonifier tip, thereby eliminating the significant fraction of large droplets. Therefore, the diffusion from small to large droplets would be minimized (although not eliminated). However, in the miniemulsions subjected to both 1 and 5 min of sonification, there will be a significant amount of monomer diffusion from the small to large droplets due to the presence of the large droplets in the system. The similarity of the final particle size in these systems is a direct result of this instability. Accordingly, the smaller final particle size in the miniemulsion subjected to 15 min of sonification is a consequence of the relative stability of the miniemulsion droplet distribution formed during sonification compared to the lower sonification times.

Kinetics Produced by Relatively Low Levels of Homogenization. Figure 8 shows the effect of predissolving polymer in miniemulsions stabilized with cetyl alcohol when either the Omni Mixer or 60 s of sonification is used for the high shear stage in miniemulsion formation. The effect of predissolving polymer in the miniemulsion formed from 60 s sonification is to enhance the rate of polymerization. Sonification has been shown to produce a droplet size in the unstable region observed using the CHDF by Miller et al.[8] Thus, it is suggested that the enhancement in the rate observed in the 1% polymer system sonified for 60 s is due to the preservation of the droplet number by the combination of polymer and cosurfactant. The rate of polymerization in the miniemulsions sonified for 60 s is low. This is most likely due to the relatively small number of droplets that are present in the system to be nucleated. The large volume subjected to sonification, coupled with the low sonification time, is suggested to cause an uneven application of shear to the system. Thus, there may be parts of the emulsion that have not been subjected to the maximum shear of the sonifier that will, therefore, contain relatively large droplets. Therefore, there is a significant amount of Ostwald ripening from the population of small size droplets that has been subjected to shear to the population of large sized droplets that is less affected by the sonification. This effect will cause the small droplets to disappear by diffusion and will result in a low droplet number available for polymerization. However, in the system created with the Omni Mixer, there is a more homogeneous application of the shear to the miniemulsion since homogenization lasts for 15 min. Also, the droplet size produced has been proposed to be stable. These two effects create an average droplet size that is smaller than the average size of the droplets contained in the miniemulsion created with 60 s of sonification.

Kinetics Produced by Relatively High Levels of Homogenization. Figure 9 shows the effect on the rate of polymerization of creating the miniemulsion with either 15 min of sonification or Microfluidization. It has been reported that the Microfluidizer provides the most uniform and finest droplet size of available laboratory homogenizers.[15,17] Thus, it is expected that the rate of polymerization would be greater in systems formed with the Microfluidizer compared to the sonifier. This is seen in miniemulsions that contain a small amount of predissolved polymer, but the opposite effect is seen in miniemulsions not containing predissolved polymer. It is suggested that this is the result of the instability that was measured by Miller et al.[8] with the CHDF. In the miniemulsion systems containing 1% polymer, the droplet number created by the homogenizers is preserved by the presence of both the polymer and cetyl alcohol. However, in the system not containing polymer, the cetyl alcohol alone is unable to preserve the initial droplet number formed during homogenization. Thus, the droplet number available for polymerization when the initiator is added to the miniemulsion is different than the droplet number immediately after homogenization. Furthermore, it appears either (1) the finer droplets produced by the Microfluidizer are more unstable than the monomer droplets produced by sonificiation or (2) there is a greater number of smaller droplets in the distribution produced during homogenization by the Sonifier than the Microfluidizer (although the overall droplet size is greater in the Sonifier than the Microfluidizer).

Ramifications on "Enhanced Droplet Nucleation". The results presented in this paper clearly show that the droplet size produced during homogenization has a strong influence on miniemulsion kinetics. Specifically, the kinetic phenomenon of "enhanced droplet nucleation" only occurs when polymer is predissolved in miniemulsions that are subjected to homogenization that produces droplet sizes that have been measured by CHDF to be in the unstable regime. When the Omni Mixer was used to create an average droplet size in the stable region observed by the CHDF, there is no enhancement in the rate of polymerization or number of droplets nucleated by predissolving polymer into the miniemulsion. This is further evidence that the dominant mechanism causing "enhanced droplet nucleation" is the preservation of the droplet number by the presence of polymer in each of the initial droplets.

Conclusions

This paper presented results on the kinetics of polymerization of miniemulsions created using cetyl alcohol as the cosurfactant and applying different levels of homogenization. It was noted that as the sonification time increased (and thus the droplet number), the rate of polymerization and number of droplets nucleated increased in systems containing either 1% predissolved polymer or no predissolved polymer. This was taken as evidence that the miniemulsion kinetics are directly related to the droplet number. Also, in these systems, the rate of polymerization for the systems containing predissolved polymer was always significantly greater than the comparable system not containing predissolved polymer. Similar behavior was reported for miniemulsions formed using the high shear Microfluidizer. However, when the low shear Omni Mixer was used for homogenization, there was no significant enhancement in the rate of polymerization or number of droplets nucleated brought about by predissolving polymer into the miniemulsion. These experiments were compared to droplet stability measurements reported in the literature. It was suggested the droplets prepared using the low shear homogenizer (Omni Mixer) were stable, while the droplets created using the high shear homogenizers (Microfluidizer and Sonifier) were relatively unstable. Since "enhanced droplet nucleation" only occurs in systems with unstable droplets, this effect was taken as further evidence that the dominant cause for "enhanced droplet nucleation" is the preservation of the monomer droplet number by the presence of polymer.

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